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Spectrophotometric determination of nickel by adsorption of nickel dimethylglyoximate on naphthalene

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Adsorption of nickel dimethylglyoximate on naphthalene was successfully applied to the determination of microamounts of nickel. To about 40 ml of sample solution containing 1-9 ml of 20 ppm nickel solution were added 1.0 ml of 0.5% dimethylglyoxime in ethanol and 2.0 ml of buffer solution to adjust the pH to 6.0-11.0. The solution was mixed thoroughly, and 4.0 ml of 10% naphthalene in acetone were added. After shaking vigorously for about 1 min, the mixture of the nickel complex and naphthalene crystals was filtered off on a sintered-glass disc and then dried. The red crystals were dissolved in chloroform, the resulting yellow solution was diluted to 10 ml, and its absorbance was measured at 375 nm against the reagent blank. The molar absorptivity of the nickel complex at 375 nm was 3.2×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$, the sensitivity being 0.019 $\mu g/cm^2$ per 0.001 of the absorbance. The coefficient of variation for the determination of 100 μg of nickel was 1.2% (10 determinations). Various alkali metal salts and metal ions, except for EDTA, did not interfere with the determination.

1 Introduction

Dimethylglyoxime, one of the α-dioximes, has been widely employed for the gravimetric and solvent extraction-spectrophotometric determination of the trace amounts of nickel or palladium.

We have been studing a new method involving the adsorption of the metal complexes on naphthalene and have already applied it to the determination of trace nickel[1)] with α-furildioxime as the complex-forming reagent. In the present communication, a dimethylglyoxime was chosen as a significant complex-forming reagent for the determination of trace nickel. This reagent forms a water-insoluble red complex with nickel, which is quantitatively adsorpted as the nickel complex on microcrystalline naphthalene at room temperature. The mixture of the

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complex and crystals is dissolved in chloroform, and its absorbance is measured at 375 nm. This method can be successfully applied for the analysis of trace nickel, as well as chloroform and naphthalene methods.

2 Experimental method

2.1 Reagents

Standard nickel solution, 20 ppm. Prepared by diluting standard nickel solution (1000 ppm, Wako Pure Chemical Industries LTD, Osaka, Japan) to 1000 ml with water.

Dimethylglyoxime solution, 0.5%. Prepared by dissolving 0.5 g of dimethylglyoxime in 100 ml of ethanol.

Buffer solutions were prepared by mixing suitable amounts of 1M acetic acid and 1M ammonium acetate solution at pH 3-6, or 1M ammonia water and 1M ammonium acetate solution at pH 8-11.

All other solutions were prepared with analytical reagent-grade chemicals by using deionized water.

2.2 Apparatus

A Hitachi Model 200-20 double beam spectrophotometer was used for the absorbance measurements with 10 mm glass cells. The pH measurements were made with a Toa-Dempa Model HM-5A, pH meter, equipped with combined glass and calomel electrodes.

2.3 Procedure

A series of sample solutions was prepared containing 1-9 ml of 20 ppm nickel solution, 2.0 ml of the buffer solution(pH 9.5) and 1.0 ml of 0.5% dimethylglyoxime solution in about 50 ml of total volume. Mix the solutions well and stand for 5 min at room temperature. After 4.0 ml of 10% naphthalene-acetone solution were added, the mixing solutions were shaken for 1 min vigorously. Filter them through a funnel attached with a disc-shaped filter(No. 5C, filter paper) by aspiration. Wash with water and dry in a dryer. Then dissolve them in chloroform and make up to 10 ml. Measure the absorbances of the solutions in 10 mm glass cells against the reagent blank prepared similarly.

3 Results and discussion

3.1 Absorption spectra

Nickel in the sample solution containing 100 μg of nickel was adsorpted on microcrystalline naphthalene as the nickel complex. The mixture of the complex and naphthalene was dissolved in chloroform , and the absorbance of the solution was measured at various wavelengths between 330 and 470 nm. The result obtained is shown in Fig.1.

The absorption curve of the nickel complex has two maximum peaks at 375 and 425 nm, while that of the reagent blank does not show any appreciable absorption at longer wavelengths above 340 nm. Therefore, 375 nm was adopted as the optimum wavelength for the absorbance measurement.

3.2 Effect of pH

According to the recommended procedure, sample solution containing 100 μg of nickel and 1.0 ml of 0.5% dimethylglyoxime solution was adjusted in the pH range of 4.5-11.0 by adding respective buffer solution. Then the adsorption of the complex was carried out with microcrystalline naphthalene at room temperature. The adsorpted mixture of the complex and crystals was dissolved in chloroform and its absorbance was measured. The pH of the solution was measured after adsorption. Figure 2 shows the effect of the pH on the absorbance. The absorbance starts from pH 4.5, sharply increases with increasing pH and reaches almost constant and maximum at pH 5.8-11.0. Therefore, the pH of the solution was adjusted to 9.5 for the absorbance measurement.

3.3 Effect of reagent concentration

To sample solution containing 100 μg of nickel and 2.0 ml of the buffer solution(pH 9.5) in total volume of approximately 50 ml, 0.1-5.0 ml of 0.5% dimethylglyoxime solution was added, and the adsorption was carried out according to the recommended procedure. Figure 3 shows the effect of the amounts of dimethylglyoxime on the absorbance. From

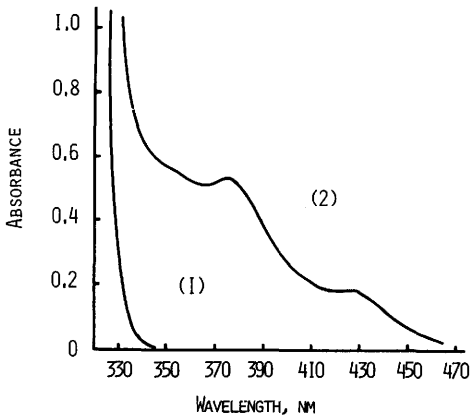

FIG. I ABSORPTION SPECTRA OF DIMETHYLGLYOXIME AND NICKEL COMPLEX IN NAPHTHALENE-chloroform
NI : 100 μG ; 0.5% DIMETHYLGLYOXIME : 1.0 ML ; PH : 9.5 ; 10% NAPHTHALENE-ACETONE : 4.0 ML ; REFERENCE : WATER ; (I) REAGENT BLANK , (2) NICKEL COMPLEX

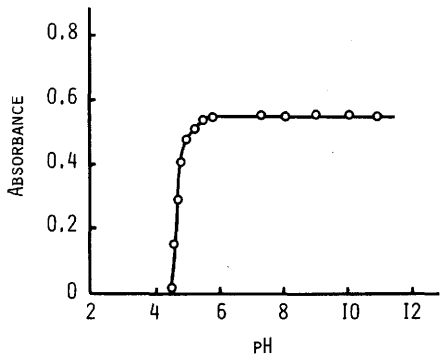

FIG. 2 EFFECT OF PH
NI : 100 μG ; WAVELENGTH : 375 NM ; 0.5% DIMETHYLGLYOXIME : 1.0 ML ; 10% NAPHTHALENE-ACETONE : 4.0 ML ; DIGESTION TIME : 5 MIN ; SHAKING TIME : 1 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK

the experimental result, the absorbance increased sharply with increasing amounts of the reagent up to 0.1 ml of 0.5% dimethylglyoxime solution and remained almost constant between 0.1 and 1.0 ml. When 5.0 ml of this solution were added, the absorbance decreased by less than 5%. Therefore, 1.0 ml of 0.5% dimethylglyoxime solution was added for the absorbance measurement.

3.4 Effect of buffer solution

Figure 4 shows the effect of addition of the buffer solution(pH 9.5) on the absorbance of the complex. The addition of 0.5-5.0 ml of the buffer solution gave no effect on the absorbance. Therefore, 2.0 ml of the buffer solution were taken for the absorbance measurement.

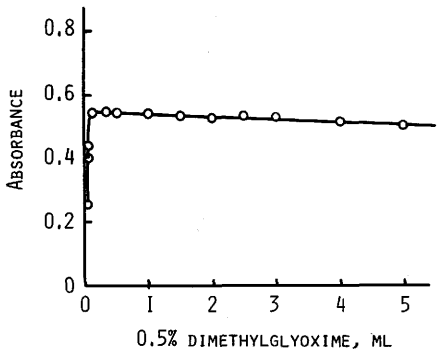

FIG. 3 EFFECT OF REAGENT CONCENTRATION
NI : 100 μG ; PH : 9.5 ; WAVELENGTH : 375 ; 10% NAPHTHALENE-ACETONE : 4.0 ML ; SHAKING TIME : 1 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK

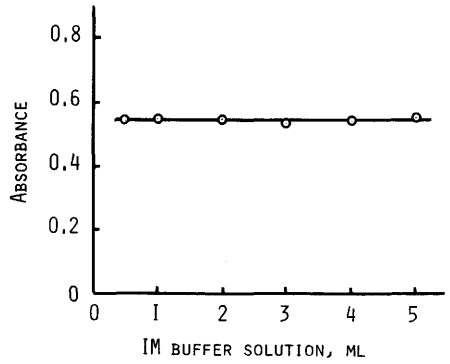

FIG. 4 EFFECT OF BUFFER SOLUTION
NI : 100 μG ; 0.5% DIMETHYLGLYOXIME : 1.0 ML ; PH : 9.5 ; WAVELENGTH : 375 NM ; DIGESTION TIME : 5 MIN ; SHAKING TIME : 1 MIN
REFERENCE : REAGENT BLANK

3.5 Effect of naphthalene concentration

The varying amounts of naphthalene were added to the solution containing 100 μg of nickel, 1.0 ml of 0.5% dimethylglyoxime solution and 2.0 ml of the buffer solution, and the adsorption of the complex was carried out. Figure 5 shows the effect of the addition of naphthalene solution on the absorbance. The addition of 3-7 ml of 10% naphthalene-acetone solution gave little effect on the absorbance, and the absorbance decreased gradually when 7-14 ml of this solution were added. Therefore, 4 ml of 10% naphthalene solution were taken for the absorbance measurement.

3.6 Effect of digestion time

The nickel complex in the solution containing 100 μg of nickel was digested at room temperature, and the effect of digestion time of the

complex on the absorbance was studied. From the experimental result, the formation of the complex was very fast, and the digestion was found to be unnecessary. Therefore, 2 min of digestion time was chosen for the absorbance measurement.

3.7 Effect of shaking time

4.0 ml of 10% naphthalene-acetone solution were added to the solution containing the nickel complex and the adsorption of the complex was performed according to the recommended procedure. Figure 6 shows the effect of shaking time on the absorbance. No change was seen in the degree of adsorption when the shaking time was varied from 3 to 180 seconds. Therefore, 60 seconds were chosen as shaking time for the absorbance measurement.

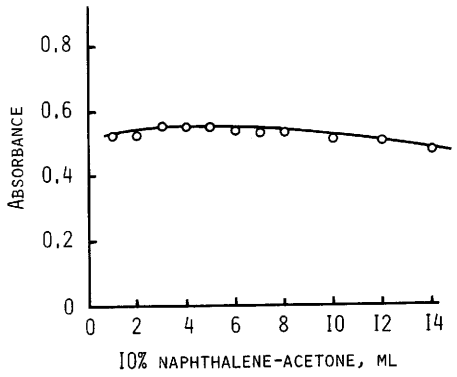

FIG. 5 EFFECT OF NAPHTHALENE CONCENTRATION
Ni : 100 μG ; pH : 9.5 ; WAVELENGTH : 375 NM ; 0.5% DIMETHYLGLYOXIME : 1.0 ML ; BUFFER SOLUTION : 2.0 ML ; SHAKING TIME : 1 MIN
REFERENCE : REAGENT BLANK

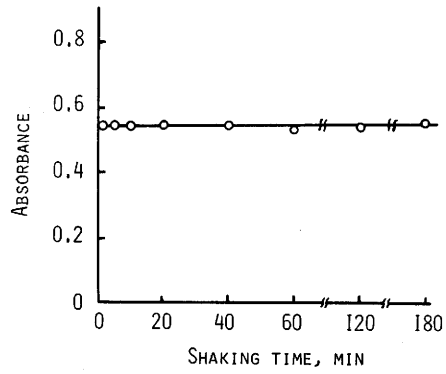

FIG. 6 EFFECT OF SHAKING TIME
Ni : 100 μG ; pH : 9.5 ; WAVELENGTH : 375 NM ; 0.5% DIMETHYLGLYOXIME : 1.0 ML ; DIGESTION TIME : 5 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK

3.8 Effect of volume of aqueous phase

The volume of aqueous phase containing 100 μg of nickel, 2.0 ml of the buffer solution (pH 9.5) and 1.0 ml of 0.5% dimethylglyoxime solution was varied from 50 to 1000 ml, and the adsorption of the complex was performed by vigorous shaking according to the recommended procedure. Figure 7 shows the effect of volume of aqueous phase on the absorbane. The absorbance decreased gradually with increasing volume of aqueous phase.

3.9 Effect of standing time

The mixture of the complex and naphthalene crystals was dissolved in chloroform, and the effect of standing time on the absorbance of the chloroform solution was investigated between 5 and 120 min. The result

is shown in Fig. 8. The complex in naphthalene-chloroform solution is very stable and the change of the color was not almost recognized. Therefore, 10 min of standing time were chosen for the absorbance measurement.

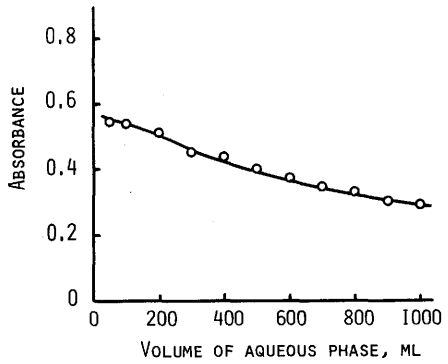

FIG. 7 EFFECT OF VOLUME OF AQUEOUS PHASE
NI : 100 μG ; WAVELENGTH : 375 NM ; PH : 9.5 ; 0.5% DIMETHYLGLYOXIME : 1.0 ML ; 10% NAPHTHALENE-ACETONE : 4.0 ML ; DIGESTION TIME : 2 MIN
REFERENCE : REAGENT BLANK

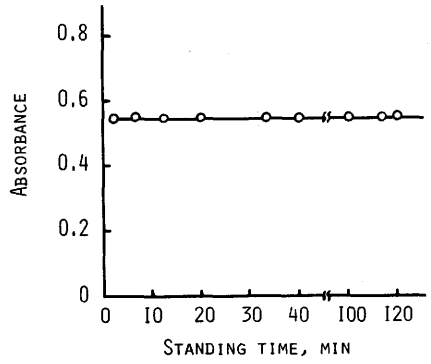

FIG. 8 EFFECT OF STANDING TIME
NI : 100 μG ; 0.5% DIMETHYLGLYOXIME : 1.0 ML ; PH : 9.5 ; WAVELENGTH : 375 NM ; SHAKING TIME : 1 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK

3.10 Calibration curve

With the optimum conditions described above, the calibration curve for nickel determination was established at 375 nm against the reagent blank. The result is shown in Fig. 9. It was linear over the range of 10-186 μg of nickel in 10 ml of chloroform. The molar absorptivity was calculated to be 3.2×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$, the sensitivity being 0.019 μg of nickel per cm^2 for the absorbance of 0.001. Ten sample solution containing 100 μg of nikel, prepared by the recommended procedure, gave a mean absorbance of 0.540 with a relative standard deviation of 1.2%.

3.11 Effect of diverse ions

The solutions containing 100 μg of nickel were prepared with varying amounts of the diverse ions and salts, and the determination of nickel was performed. Some of the results are given in Tables 1 and 2. One hundred micrograms of bismuth gave no interference, but 200 μg of it did. Especially, even a small amount of EDTA gave serious negative interference. Other diverse metal ions and salts did not interfere with determination of nickel.

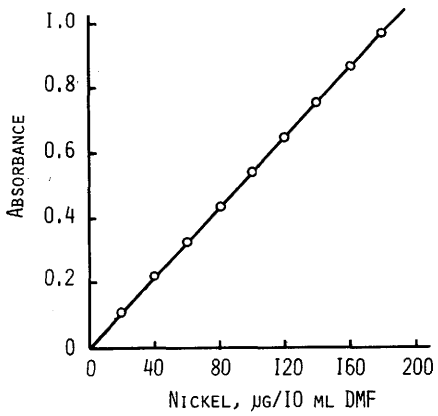

Fig. 9 Calibration curve for nickel
Wavelength : 375 nm ; 0.5% dimethylglyoxime : 1.0 ml ; pH : 9.5 ; 10% naphthalene-acetone : 4.0 ml ; Digestion time : 2 min ; Shaking time : 1 min
Reference : Reagent blank

Table 1 Effect of alkali salts

Alkali salts	Amount added(mg)	Absorbance(375 nm)
—	—	0.540
Na_2SO_4	100	0.542
"	500	0.548
CH_3COONH_4	100	0.545
"	500	0.550
NaCl	100	0.535
"	500	0.550
NH_4Cl	100	0.546
"	500	0.538
$(NH_4)_2C_2O_4 \cdot H_2O$	100	0.532
"	500	0.540
NaH_2PO_4	100	0.555
"	500	0.545
K_2HPO_4	100	0.548
"	500	0.532
KNO_3	100	0.545
"	500	0.549
KBr	100	0.548
"	500	0.543
CH_3COONa	100	0.545
"	500	0.548

Sodium citrate	100	0.539
"	500	0.519
Sodium tartrate	100	0.537
"	500	0.548
EDTA	2	0.002

Nickel : 100 μg, pH : 9.5, Naphthalene : 0.4 g

Table 2 Effect of diverse metal ions

Metal ions	Ion added(μg)	Absorbance(375 nm)
—	—	0.540
Pb^{2+}	100	0.530
"	200	0.550
Fe^{3+}	100	0.535
"	200	0.502
Cu^{2+}	100	0.534
"	200	0.530
Co^{2+}	100	0.528
"	200	0.532
"	300	0.548
Zn^{2+}	100	0.551
"	200	0.540
Cd^{2+}	100	0.546
"	200	0.538
Mn^{2+}	100	0.535
"	200	0.551
Cr^{6+}	100	0.548
"	200	0.547
"	300	0.560
Bi^{3+}	100	0.551
"	200	0.588
"	300	0.623

Ni : 100 μg, pH : 9.5, Naphthalene : 0.4 g

Reference

1) M. Satake, Y. Matsumura, T. Fujinaga, Y. Takagi, Bunseki Kagaku, 27, 486 (1978).